

Peierls Mechanism of the Metal-Insulator Transition in Ferromagnetic Hollandite $\text{K}_2\text{Cr}_8\text{O}_{16}$

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Synchrotron X-ray diffraction experiment shows that the metal-insulator transition occurring in a ferromagnetic state of a hollandite $\text{K}_2\text{Cr}_8\text{O}_{16}$ is accompanied by a structural distortion from the tetragonal $I4/m$ to monoclinic $P112_1/a$ phase with a $\sqrt{2} \times \sqrt{2} \times 1$ supercell. Detailed electronic structure calculations demonstrate that the metal-insulator transition is caused by a Peierls instability in the quasi-one-dimensional column structure made of four coupled Cr-O chains running in the c -direction, leading to the formation of tetramers of Cr ions below the transition temperature. This furnishes a rare example of the Peierls transition of fully spin-polarized electron systems.

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Low-dimensional solids have attracted considerable attention in recent years. An interesting class of these materials, which is just started to be explored, are the so-called tunnel compounds. Typically, they are made of double MO chains (M is, e.g., a transition-metal element) with edge-sharing MO_6 octahedra, forming zigzag chains (triangular ladders). These double chains are connected *via* corner-sharing octahedra into particular structures, e.g., hollandites, ramsdellites, romanachites, todorokites, or systems with the calcium-ferrite structure. The large tunnels thus formed are filled by ions such as K^+ , Rb^+ , Ca^{2+} , Ba^{2+} , etc. These materials display a wide range of magnetic, charge, and orbital orderings, metal-insulator transitions (MIT), etc [1–4]. They are usually considered as quasi-one-dimensional (1D), the 1D building blocks being the double chains [4, 5].

Perhaps the most surprising phenomenon was discovered recently in a Cr hollandite $\text{K}_2\text{Cr}_8\text{O}_{16}$ [2]. This material, which is tetragonal (space group $I4/m$) [6] and metallic at room temperature, becomes ferromagnetic below $T_c = 180$ K, but at lower temperatures, it experiences an MIT at $T_{\text{MI}} = 95$ K, remaining ferromagnetic in the insulating phase. This is very unusual: typically, insulating transition-metal oxides are antiferromagnetic, and ferromagnetism usually goes hand in hand with metallicity [7]. Among the several explanations offered, a proposal was made that charge ordering is responsible for the low-temperature behavior [8].

The clue to understanding the nature of MIT in $\text{K}_2\text{Cr}_8\text{O}_{16}$ can be obtained from structural studies, which should show the signatures of eventual charge or orbital order, or some other structural distortions. Conventional powder X-ray studies [2] did not detect any structural

distortions, which nevertheless should be present. Therefore, in the present study, we undertook careful structural determination, using synchrotron radiation, and we combined it with the detailed electronic structure calculations to obtain a complete picture of the phenomena occurring in $\text{K}_2\text{Cr}_8\text{O}_{16}$ at the MIT.

The picture which emerged out of our study is rather unexpected: one can indeed consider this material as quasi-1D, but the 1D building blocks are not the usually considered double chains, but rather the four corner-sharing chains around small squares, forming vertical “chimneys” in the c -direction (columns Cr1-Cr2-Cr3-Cr4 in Fig. 1). To the best of our knowledge, this is the first example of the 1D structure made in such a way. The MIT in $\text{K}_2\text{Cr}_8\text{O}_{16}$ is caused by the Peierls instability in this four-chain column. This mechanism provides a natural explanation for the observed structural distortions, i.e., the lattice dimerization in each of the four-chain columns below T_{MI} . Importantly, we detected no charge ordering at the MIT; charge density is found to be the same at all Cr ions.

The synchrotron X-ray diffraction experiment was carried out on the imaging-plate diffractometer at beamlines 8A and 8B of Photon Factory in KEK. The reflection data sets for the structural analysis on single crystals were collected in the ferromagnetic metallic (FM) and ferromagnetic insulating (FI) phases using the X-ray energy of 18 keV [9].

To elucidate the origin of the FI phase, the crystal structure was explored by oscillation photographs. Superstructure reflections associated with the unit cell of $\sqrt{2}a \times \sqrt{2}b \times c$ were clearly observed in the FI phase (20 K). The intensity of the superlattice reflections is

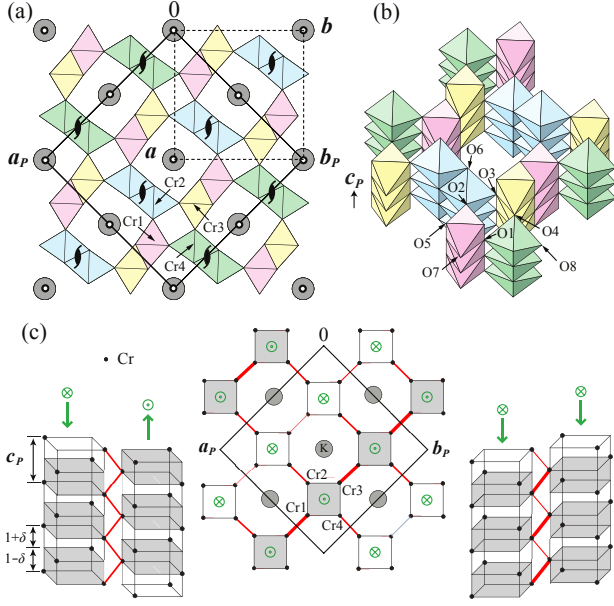


FIG. 1: (Color online) (a) Crystal structure of $\text{K}_2\text{Cr}_8\text{O}_{16}$ at 20 K viewed down the c -axis and (b) perspective view showing the connection of the double Cr chains running in the c -direction. The structures are drawn with the CrO_6 octahedra. In (a), the unit cells of the FM and FI phases are indicated by dotted and solid lines, respectively, and the inversion centers and two-fold screw axes are indicated by open circles and solid symbols, respectively. (c) Schematic illustration of the FI phase, emphasizing the four-chain columns with the lattice dimerization, as indicated by shadow. Red lines mark double zigzag chains. The four-chain columns with \uparrow/\downarrow dimerization (indicated by \oplus/\otimes) are arranged in a stripe-like pattern.

$\sim 10^{-3}$ of the fundamentals, continuously increasing with decreasing temperature, suggesting a second-order phase transition. The distribution and intensity of the superlattice reflections are consistent with the Laue class $2/m$; although peak splittings due to distortion of the lattice from 90 degree were not observed, the intensities of equivalent/inequivalent superlattice reflections showed $I(hkl) = I(\bar{h}\bar{k}\bar{l}) \neq I(\bar{k}hl) = I(kh\bar{l})$ with the monoclinic domain ratio of 6 : 4. Thus, the system is monoclinic in the FI phase. From a detailed analysis of the reflection conditions [9], we concluded that the space group of the FI phase is $P112_1/a$. The transition is accompanied by a symmetry breaking with the loss of the four-fold axis and the mirror plane perpendicular to the c -axis.

The structure analysis of the FI phase was performed on the basis of the space group $P112_1/a$, where four Cr sites, two K sites, and eight O sites become crystallographically inequivalent [9]. From the result, we nevertheless found that the Cr valences estimated from the bond valence sum are the same at all the Cr sites within the experimental error ($\lesssim 0.03$ electrons/Cr); i.e., no evidence of charge ordering. The resulting crystal structure of the FI phase is shown in Fig. 1.

The observed structural distortions can be explained as follows: The four Cr sites form three types of double chains (Cr1-Cr3, Cr2-Cr2, and Cr4-Cr4 double chains, see Fig. 1(a)), a half of which (Cr1-Cr3) has a Cr-Cr bond alternation. Simultaneously, there occurs a lattice dimerization in all the four-chain columns made of Cr1-Cr2-Cr3-Cr4 chains, leading to the formation of tetramers of Cr ions (shown in Fig. 1(c) by shading). This dimerization takes place within the unit cell in the c -direction, without doubling the c lattice parameter. The degree of dimerization is $\delta = 0.025$ at 20 K, where δ is defined in Fig. 1 and is zero in the FM phase. As we show below, it is this lattice dimerization in the four-chain columns which plays a crucial role and drives the structural and metal-insulator transition. The relative stacking of column distortions is in such a way that they form stripes in the a_P direction (see Fig. 1(c), middle), with the distortions in-phase along these stripes, but opposite (shifted by a half of the period) in the neighboring stripes. This leads to the net monoclinic symmetry. This also explains the occurrence of the bond alternation in the double chains made of Cr1-Cr3 in these stripes (see Fig. 1(c), right), but no dimerization in double chains made of Cr2-Cr2 and Cr4-Cr4 which are sandwiched between the stripes with opposite distortions (Fig. 1(c), left).

To clarify the mechanism of the MIT further, we carried out the electronic structure calculations using different methods: local-density approximation (LDA) and generalized gradient approximation (GGA), taking into account the Hubbard-type repulsion (LDA/GGA+ U), in the FLAPW [10] and LMTO-ASA [11] implementations. The double counting corrections were taken in form of the fully localized limit [12] both for the FLAPW and LMTO-ASA calculations. We also checked the around-mean-field correction [12] in the FLAPW calculation and confirmed that the results are almost the same. We also note that the value $U \simeq 2 - 3$ eV we used is standard and accepted for Cr oxides with Cr^{3+} and Cr^{4+} [13, 14]; we actually confirmed that the results do not change qualitatively for different values of U between 2 and 5 eV.

We then found that the electronic structure of the high-temperature phase is that of a half-metal, but with the substantial dip, almost a pseudogap at the Fermi level (see Ref. [15] for the result at $U = 0$ eV). Thus, one may anticipate that relatively minor changes in structure can push the occupied states down and empty states up, opening a gap in the spectrum and giving the gain in energy. This is indeed what happens in $\text{K}_2\text{Cr}_8\text{O}_{16}$: as shown in Fig. 2(a)-(d), the calculations using the experimentally observed structure of the FI phase show that a gap of $0.03 - 0.13$ eV opens, depending on the value $U = 2 - 3$ eV. This is in reasonable agreement with the gap ~ 40 meV found recently by laser photoemission [16].

Our calculations confirmed that the ground state of $\text{K}_2\text{Cr}_8\text{O}_{16}$ is ferromagnetic both in the metallic and in the insulating phase. Calculations of the exchange coupling

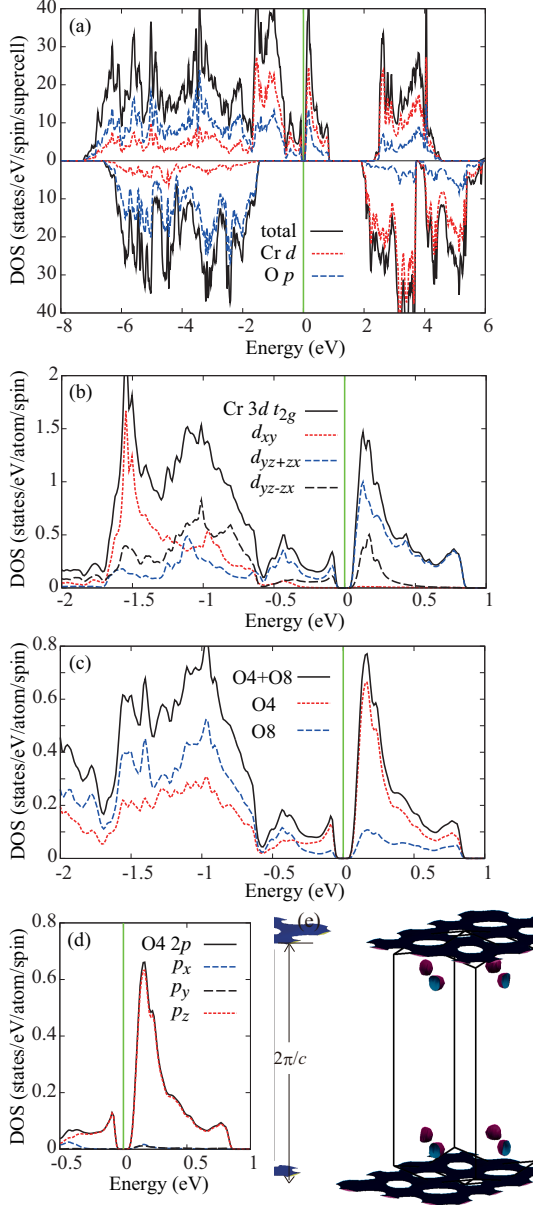


FIG. 2: (Color online) Calculated GGA+ U partial DOS in the FI phase of $\text{K}_2\text{Cr}_8\text{O}_{16}$ at $U = 3$ eV: (a) the majority- and minority-spin DOS in a wide energy range, (b) the majority-spin $3d\ t_{2g}$ orbitals of Cr4, (c) the majority-spin $2p$ orbitals of corner (O4) and edge (O8) oxygens, and (d) the orbital decomposition for the majority-spin band of O4. The Fermi level is indicated by a vertical line. In (e), the calculated Fermi surface in the FM phase at $U = 2.9$ eV is shown.

constants using the procedure of Ref. [17] demonstrate that all the exchange integrals between nearest-neighbor Cr ions are indeed ferromagnetic, where, surprisingly, the strongest Cr-Cr coupling is not that in the double chains, but that *between* the double chains, *via* corner-shared oxygens (O1, O2, O3, and O4): in the metallic state, the values are $J \sim 5.3$ meV in the double chain, but

twice as large between the double chains, ~ 10.6 meV. The mechanism of ferromagnetism here is similar to that in CrO_2 [14] and is in fact due to a double exchange [15]. Indeed, one electron with the symmetry d_{xy} in the local coordinate system of Fig. 3 (with the z -axis directed towards the corner oxygen connecting double chains) is practically localized, whereas the remaining electrons are in delocalized states formed by the d_{yz} and d_{zx} orbitals [15, 18]. The opening of a small gap (~ 0.1 eV) at the Fermi level in the low-temperature phase, which is much smaller than the bandwidths ~ 2 eV, does not significantly modify the exchange mechanism.

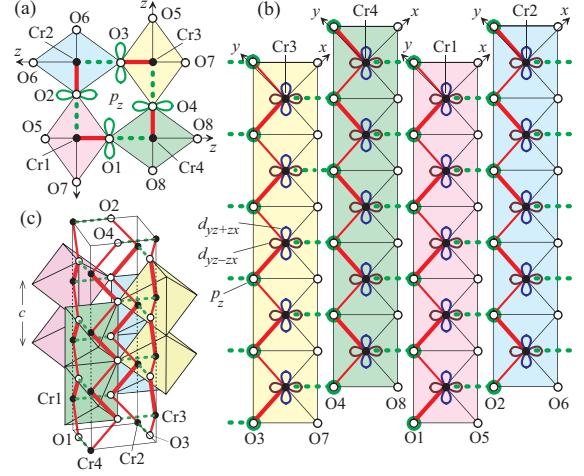


FIG. 3: (Color online) (a) The four-chain column viewed down the c -axis, (b) unfolded four-chain column, and (c) side view of the four-chain column. The shorter and longer bonds due to the lattice dimerization are indicated by thick and thin lines, respectively. Orbitals $d_{yz\pm zx}$ of Cr ions and p_z of corner oxygens (O1, O2, O3, and O4) are also shown in the local coordinate axes (x, y, z).

The stronger coupling between the corner-sharing Cr ions of different double chains is clear from the orbital-projected density of states (DOS) shown in Fig. 2(b)-(d); the states at the Fermi level are predominantly made up of the d_{yz} and d_{zx} orbitals of Cr with strong admixture of the p_z orbitals of corner oxygens (O4) connecting two double chains, reflecting a negative charge-transfer-gap situation [15]. Thus, it is natural to treat $\text{K}_2\text{Cr}_8\text{O}_{16}$ as consisting primarily of strongly coupled four corner-sharing Cr chains. In this sense, $\text{K}_2\text{Cr}_8\text{O}_{16}$ can in the first approximation be treated as a quasi-1D system, but with the 1D blocks quite different from what is usually assumed in the tunnel compounds of this type.

The quasi-1D character of the electronic states is further confirmed by the Fermi surface calculated in the FM phase (see Fig. 2(e)); the result also serves as the explanation of the nature of the MIT in this system. As one sees from Fig. 2(e), there exists strong nesting in the elec-

tron spectrum, with the nesting wave vector $Q_z = 2\pi/c$. Correspondingly, we may expect that there will occur a Peierls transition in this system. The structural data presented above agree with this picture: they demonstrate that indeed a lattice dimerization in the c -direction corresponding to Q_z occurs, after which the tetramers of Cr ions are formed in the four-chain columns. This opens a gap at the Fermi level, but, as there are four Cr ions in a four-chain column per unit cell in the c -direction, it does not double the unit cell along c . On the other hand, the arrangement of these distorted four-chain columns leads to an increase of the unit cell in the ab -plane, with the unit cell becoming $\sqrt{2} \times \sqrt{2} \times 1$.

The presence of 1D columns consisting of four Cr chains explains the existence of a Peierls transition for the average valence $\text{Cr}^{3.75+}$ in $\text{K}_2\text{Cr}_8\text{O}_{16}$. This value, with one extra electron per four Cr ions on top of the Cr^{4+} background, seems at first glance to be unfavorable for Peierls dimerization. However, for the 1D system of four chains, the spectrum for undimerized case has four fully spin-polarized bands near the Fermi level, touching at band edges (see Fig. 5 of Ref. [15] for the bands at $U = 0$ eV), i.e., without a gap, but with the lowest band filled and 3 upper bands empty. The Peierls dimerization opens a gap between these bands.

A tight-binding band calculation for an isolated column shown in Fig. 3 corroborates this picture; the calculation with the $d_{yz\pm zx}$ of Cr ions and p_z orbitals of corner oxygens (O1, O2, O3, and O4), which are connected by π bond, roughly reproduced the topmost four t_{2g} bands of the GGA+ U band structure. Thus, the band structure near the Fermi level is indeed surprisingly simple. The band gap opens in this tight-binding band structure when the Cr-O bond alternation observed experimentally in the FI phase was introduced. Thus, the average valence $\text{Cr}^{3.75+}$ and the 1D columns made of four chains perfectly match, leading to a Peierls instability without any charge ordering.

Finally, let us remark that the MIT due to Peierls distortion in a system of fully spin-polarized electrons, which leads to an uncommon FI phase of materials, is a very rare phenomenon. This effect is connected with the specific feature of the electronic structure of $\text{K}_2\text{Cr}_8\text{O}_{16}$, where the 1D objects in it are not the simple 1D chains but the four-chain columns. Usually, the Peierls distortion corresponds to a formation of valence bonds and requires the presence of both spin-up and spin-down electrons, whereas in the present case, we found that a similar effect can occur in a system of fully spin-polarized electrons. In fact, it turned out that, in the present system, the electrons of only one spin close to the Fermi level determine the type of distortion and opening of the gap due to gain in kinetic (or band) energy via the Peierls mechanism, although the electron correlations among both-spin electrons are definitely important for preparing the state with a Peierls instability, i.e., the FM state of the

double-exchange origin. We may therefore say that the present MIT is realization of a unique Peierls transition of fully spin-polarized electrons (or “spinless” fermions) where the spin degrees of freedom of electrons essentially play no role in the transition itself.

In conclusion, we made the synchrotron X-ray diffraction experiment on the low-temperature FI phase of $\text{K}_2\text{Cr}_8\text{O}_{16}$ and reported the structural changes causing the MIT of this material. The structural distortions observed consist of dimerization in the four-chain columns of corner-sharing CrO_6 octahedra and formation of a stripe-like pattern of the dimerized columns. These structural data, together with our electronic structure calculations, lead us to a model of the MIT in this system caused by the Peierls transition in the quasi-1D four-chain columns, which form the natural 1D building blocks. The 1D units in $\text{K}_2\text{Cr}_8\text{O}_{16}$ are thus different from the usually considered double chains. The system remains ferromagnetic in the FI phase; the double-exchange ferromagnetism is not altered by the opening of the small gap. We thus demonstrated that the uncommon FI phase of materials can be realized in $\text{K}_2\text{Cr}_8\text{O}_{16}$ via the MIT due to Peierls mechanism in a system of fully spin-polarized electrons, which is indeed a very rare phenomenon. Besides specific importance for $\text{K}_2\text{Cr}_8\text{O}_{16}$, our results demonstrated that, in tunnel compounds like hollandites and similar materials, the coupling between the double chains via corner-shared oxygens may be as strong, and sometimes even stronger than that within these chains. This result may change the usual interpretation of the properties of the whole big class of these materials, which may have general and important implications for future researches.

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- [1] M. Isobe, S. Koishi, N. Kouno, J. Yamaura, T. Yamauchi, H. Ueda, H. Gotou, T. Yagi, and Y. Ueda, J. Phys. Soc. Jpn. **75**, 73801 (2006).
 - [2] K. Hasegawa, M. Isobe, T. Yamauchi, H. Ueda, J.-I. Yamaura, H. Gotou, T. Yagi, H. Sato, and Y. Ueda, Phys. Rev. Lett. **103**, 146403 (2009).
 - [3] K. Yamaura, M. Arai, A. Sato, A. B. Karki, D. P. Young, R. Movshovich, S. Okamoto, D. Mandrus, and E. Takayama-Muromachi, Phys. Rev. Lett. **99**, 196601 (2007).
 - [4] O. Pieper, B. Lake, A. Daoud-Aladine, M. Reehuis, K. Prokeš, B. Klemke, K. Kiefer, J. Q. Yan, A. Niazi, D. C. Johnston, and A. Honecker, Phys. Rev. B **79**, 180409(R) (2009).

- (2009).
- [5] G. W. Chern and N. Perkins, Phys. Rev. B **80**, 220405(R) (2009).
 - [6] O. Tamada, N. Yamamoto, T. Mori, and T. Endo, J. Solid State Chem. **126**, 1 (1996).
 - [7] D. I. Khomskii and G. A. Sawatzky, Solid State Commun. **102**, 87 (1997).
 - [8] P. Mahadevan, A. Kumar, D. Choudhury, and D. D. Sarma, Phys. Rev. Lett. **104**, 256401 (2010).
 - [9] See Supplementary Material for more information. Also see A. Nakao *et al.*, preprint.
 - [10] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2K* (Technische Universität Wien, Austria, 2002).
 - [11] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).
 - [12] M. T. Czyżyk and G. A. Sawatzky, Phys. Rev. B **49**, 14211 (1994).
 - [13] I. I. Mazin, Phys. Rev. B **75**, 094407 (2007).
 - [14] M. A. Korotin, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. Lett. **80**, 4305 (1998).
 - [15] M. Sakamaki, T. Konishi, and Y. Ohta, Phys. Rev. B **80**, 024416 (2009); **82**, 099903(E) (2010).
 - [16] P. A. Bhobe *et al.*, unpublished.
 - [17] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).
 - [18] M. Itoh, H. Takeda, Y. Shimizu, H. Sakurai, M. Isobe, and Y. Ueda, J. Phys.: Conf. Ser. **320**, 012070 (2011).